

# New Materials

## Atomic-Scale Architecture of Metallic Solids

by WILLIAM L. JOHNSON

The world of solid objects can be divided into two categories according to how the atoms are arranged, whether in a regular periodic array called a crystal or in some other more random structural form. The overwhelming majority of solids that you see around you are noncrystalline — our bodies, this paper, the vinyl you are probably sitting on. But nearly all metallic solids, on the other hand — steel, aluminum or any of the common metals that we're familiar with — are invariably found to occur in crystalline form. There *are* also noncrystalline metals — metallic glasses. In this article, I will discuss how these are formed, what sort of properties you would expect them to have, and how atoms in such metals are arranged.

First, how are atoms arranged in crystals? Most of us are familiar with crystals, with things like diamonds, for example, which have well-defined geometrical shapes. You can recognize a crystal by its highly symmetric form, which is due to the fact that the atoms in a solid crystal are arranged in some regular fashion — in a periodic array. This was recognized in the 19th century. In an idealized crystal, the atoms sit on a regular array of sites. We can also have material consisting of many crystals that are conjoined along what are called grain boundaries. In each separate crystal the atoms are still situated in perfect array. Most metals that we deal with in the practical world are in this polycrystalline form.

What else can happen in a metal? Things aren't always in perfect array — there can be disorder or things out of place. It's very common to have vacancies in metals. A vacancy is a lattice site where one of the atoms of the crystal is missing. The effect of a vacancy goes beyond that of just taking out an atom. Taking out one atom tends to affect those around it as well; surrounding atoms shift their positions.

In the real world few materials are pure. Most materials consist of a mixture of atoms, and there are several ways in which atoms can mix together to form a crystal. One way is a substitutional solid solution, in which a foreign

atom substitutes for a host atom in the perfect crystal. If it is bigger than the host atom and takes up a little more space, all the surrounding host atoms have to shuffle around to make room for it. So again, the influence of putting in the foreign atoms extends beyond the foreign atom itself and affects the neighboring atoms.

A second way in which foreign atoms can enter a crystal is through an interstitial solution. When the foreign atom is too small to substitute for host atoms, it can occupy instead one of the interstitial sites — the space between the host atoms of the crystal. Surrounding host atoms again react by moving away; since the interstitial site is small, they're pushed out slightly to accommodate the foreign atom.

As examples of these situations, a perfect crystal could be paralleled in the real world by a single crystal of iron. Stainless steel is a substitutional solution, and an example of an interstitial solution is carbon steel, or high strength steel.

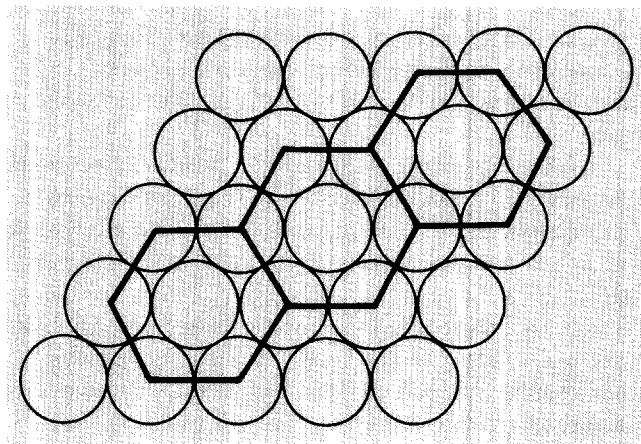
Actually, these perfect arrangements never occur in the real world either, because materials are at some finite temperature, typically ambient temperature, but sometimes higher temperatures, depending on the situation. When there is thermal energy available — that is, at higher temperatures — these atoms don't just sit at their equilibrium positions but move and rattle around somewhat. If we heat a metal hot enough and get very close to its melting point, we can still have a crystal with a periodic array of atoms, but it is now a highly agitated or disordered crystal. But when we melt a crystal, we lose that regular arrangement of atoms. In metallic glasses the atomic-scale architecture is similar to that of a liquid.

What do the atoms in a metal actually look like? Probably the best description of an atom in a metal is a round ball. That's not true of all atoms, and it's not true of metal atoms in all circumstances. The carbon atoms in a diamond are not well described as balls. They have some very specific kinds of geometrical shapes, which are de-

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fined by the way in which the atoms are bonded to their neighbors. In other words, not all atoms look round; some have very strong directionality in space. They have chemical bonds that stick out in particular directions and join them to their neighbors. Metal atoms generally don't do that. Basically, metal atoms are spherically symmetric. They have a round shape and they see their environment in a very nonpreferential and nondirectional way.

To understand why atoms in a metal arrange themselves the way they do, probably the best concept to start with is to think of how to put balls together in space to fill space most efficiently. That is, how could we take a random collection of balls and put them together to fill space in a way that would leave the least amount of unfilled volume? Let's assume we have a pure metal, iron, for example, with one kind of atom, and that we can think of it in two dimensions, even though it exists in three. The iron atoms prefer to pack themselves in a way to fill space most efficiently and consequently adopt a hexagonal close-pack geometry with each atom having six nearest neighbors.



Seen in two dimensions, the atoms of this "perfect crystal" of iron arrange themselves most efficiently by lining up with six neighbor atoms, creating a neat hexagonal symmetry.

What if we were to put foreign atoms in this perfect hexagonal crystal to form a substitutional solution? The foreign atoms that might be interesting in the case of an iron crystal would be atoms like nickel or chromium, which are the typical additions used to form various types of steels. Chromium atoms reduce the tendency of the iron crystal to oxidize, but chromium is a very expensive material and stainless steels are expensive to make.

We could also put interstitial atoms into the iron crystal. The one most commonly used is carbon, but other additions such as nitrogen and boron atoms are also used. Car-

bon atoms are considerably smaller than the iron atoms of the host matrix. The carbons tend to go interstitially and occupy the holes between iron atoms, creating steel. Steel is typically used in applications where a cheap, high-strength material is needed.

What makes steel strong? A pure piece of iron subjected to a force — say a shear force — deforms fairly easily, precisely because of its periodic arrangement. The atomic arrangement is along lines, called slip planes, along which the atoms can roll very easily. When you apply a shearing force to a perfect crystal such as iron, it will slip or deform along those planes, the atoms behaving like a string of ball bearings rolling over each other.

When you introduce carbon into the crystal, the configuration changes. Carbon is not really a metal atom. It doesn't look like a round ball; it forms chemical bonds with a strong directionality to the neighboring iron atoms. In two dimensions it looks like a little spur locked to its neighboring iron atoms. In three dimensions the carbon atoms occupy octahedral holes in the crystal, but they form the same kind of directional bonds and the same kind of considerations come into play. What the carbon atom does is prevent motion along the easy direction lines. If you try to deform this metal by pushing with a shear force, the carbon atoms will prevent the slip planes from moving with respect to each other, making steel stronger than the iron. A pure piece of iron has a strength of about 50,000 pounds per square inch (psi). With 1 percent carbon in it that typically changes to 150,000 psi. Even this small amount of carbon has a very dramatic effect on the ability of metal to resist being deformed. It increases its strength by a factor of three.

So if we wanted to make strong materials, materials that would resist wear, for example, or which would be useful in structural applications, the obvious thing to do would be to put more carbon in them. It turns out that that's not easy to do because nature is not very accommodating. The situation is similar to a common kitchen problem — dissolving salt in water. At room temperature water will dissolve only a certain amount of salt. When you try to put more salt in, it doesn't dissolve. Heating the water increases the ability to dissolve the salt. When it cools, the excess salt will crystallize out again.

Solid metals are much the same. At low temperatures, such as room temperature, the ability of iron to dissolve carbon is restricted to less than 1 percent. If you heat iron up to high temperatures, it will dissolve a little bit more carbon — about 1½ percent. If you then cool it down slowly, the carbon atoms like to leave the solution in the form of iron carbide.

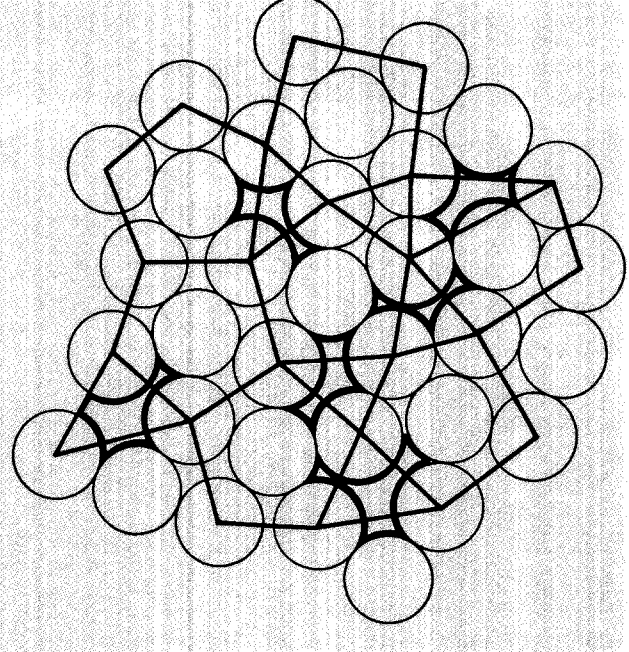
However, if you cool the iron crystal quickly enough, the carbon atoms might have too little time to find their way out. This is what a blacksmith does when he quenches a piece of iron. He loads it up with carbon by heating it in a furnace and then quenches it in water to retain the carbon. Roughly speaking, the more carbon he gets in, the stronger the material gets.

But you can only go so far. Even if you heat a piece of iron to its melting point, it still dissolves only about 1½ percent carbon. So there's a limit to how strong you can make iron by that method. In recent years scientists have found various other methods of getting around this problem by putting the carbon in by brute force; you just stuff the carbon in. One such technique is called ion implantation, in which carbon atoms are ionized, stripped of a few of their electrons, accelerated with an electrostatic field of very high energy, and then allowed to ram into the surface of the metal. Depending on its energy, the carbon can go quite a distance into the surface. But the distance is limited by the amount of energy you can give the carbon. Practical considerations restrict that. Typically in this method the surface of the iron sample becomes impregnated with a high concentration of carbon, but the carbon atoms are unable to penetrate beyond the surface.

This technique has been studied by several researchers and shown to be very effective in producing extremely hard surfaces on iron. There are applications in which only the hardness of the surface is important, for example, a very precise ball bearing. A very small amount of wear will render the ball bearing useless anyway. In this case hardening just the surface will increase the working life of the bearing.

Ion implantation is useful, but nevertheless restricted to the surface of materials. How can we beat the problem of getting carbon (or boron or nitrogen or any of these other small atoms that make iron very hard by occupying the interstitial holes) into bulk iron? In a perfect crystal the atoms arrange themselves to pack most efficiently in space. A solid metal will seek out this arrangement because it is the lowest energy state of the system. There are, however, many other ways to arrange atoms in two-dimensional or three-dimensional space that are still fairly efficient. One way is suggested by the phenomena that occur when a metal melts. A liquid metal no longer forms a lattice; it no longer packs atoms together in this highly symmetric arrangement. In a liquid metal there are many atoms that don't have six nearest neighbors; they could have just five (in two dimensions).

If we start with an atom and give it five neighbors on a perfect pentagon, we would have to conjoin that to a

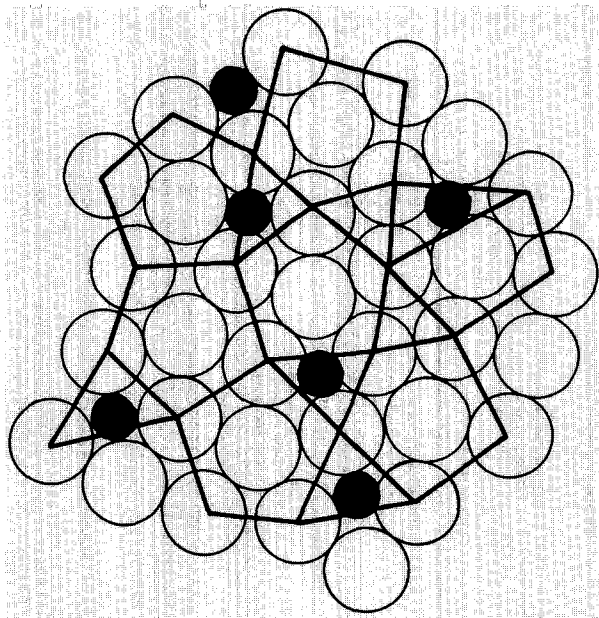


In a liquid metal, which has expanded, there will be many atoms that have only five neighbors. Conjoining five-sided figures doesn't work out as neatly as the hexagonal configuration; when you try to arrange the atoms in a regular periodic array, they fit together only by leaving holes, or defects — indicated here by the triangles between pentagons over the heavier lined spaces.

second pentagon to fill space as shown in the figure above. Then we conjoin a third pentagon (a five-fold coordinated atom) and so on. With the hexagon we get right back to where we started from, and everything works out to give a perfect crystal. When we try to do the same with five atoms, we wind up with small triangular holes left over, as seen in the figure above. In a two-dimensional array with five neighbors, these holes will always occur as a basic kind of defect.

This same problem occurs in three dimensions. To visualize our hexagonal close-pack structure in three dimensions, the six-neighbor-packed planes can simply be stacked on each other. Gold and copper crystals look exactly like this — a sequence of six-neighbor layers. In three dimensions, five-fold symmetry is obtained by placing twelve nearest neighbor atoms around a central atom to form an icosahedron, a three-dimensional object whose faces are pentagons. The holes, or defects, also occur when icosahedra are used to fill three-dimensional space. Five-fold symmetry is linked up in a very fundamental way to the formation of metallic glasses, or noncrystalline metals, because perfect crystals cannot be formed from objects which have five-fold symmetry.

You might wonder why five-neighbor arrangements would ever tend to form. Why don't metals just exist in the neat six-fold packings? Under normal conditions of thermodynamic equilibrium, where nature is left to run its course, the atoms in solid metals are always found to form periodic arrangements. Something a little different happens when a metal melts. Because of all the extra thermal energy, the atoms of the metal tend to assume a highly disordered arrangement. In liquid metals — as in liquids generally — it is possible to form five-neighbor arrangements.



The holes in the liquid five-neighbor packing offer little extra spaces to put carbon or boron atoms (dark circles), forming an alloy, here  $\text{Fe}_{80}\text{B}_{20}$  — 80% iron, 20% boron. This also stabilizes the configuration and makes it more competitive with the six-neighbor packing of the solid crystal.

Going back to our iron and carbon problem, we see an obvious way to exploit this atomic structure of liquids. A liquid will generally contain extra little spaces (or defects) in which to put carbon atoms, as shown in the figure above. In fact, liquid iron and other liquid metals can dissolve much carbon — 20 percent or more! We can't achieve that situation in a solid metal since the solid likes to seek out its lowest energy arrangement, which has six neighbors and little solubility for carbon. But carbon (or nitrogen or boron) fits nicely into the defect holes of a liquid metal. If we fill each of the triangular defects with a small atom, we have an alloy that fills space very efficiently. When these smaller atoms are added to pure iron, another effect is to lower the melting point. The liquid begins to compete a little bit more effectively with the six-fold neighbor solid state, since we have now filled space more efficiently.

But we're still in trouble, because if we cool the metal down far enough, it will still crystallize. In the case of carbon in liquid iron, the carbon will come out and form an iron carbide. It will leave the iron behind with only a little carbon and put us back where we started. If we go to low temperatures and solidify the material, we always lose the five-neighbor arrangement of things.

One factor we can work with is that atoms move at some finite velocity, so it takes them a certain amount of time to go a given distance. If we were to cool a liquid iron-boron (or carbon) solution very rapidly, so rapidly that the boron atoms didn't have time to get out, then we could possibly retain the desired kind of structure in a solid. If we succeed in that, then we can form a metallic glass, a noncrystalline metal, for example, a glass consisting of 80 percent iron and 20 percent boron (or carbon). Comparing this to the crystalline metal with only 1 or 2 percent carbon, we might expect to have produced an extremely strong material.

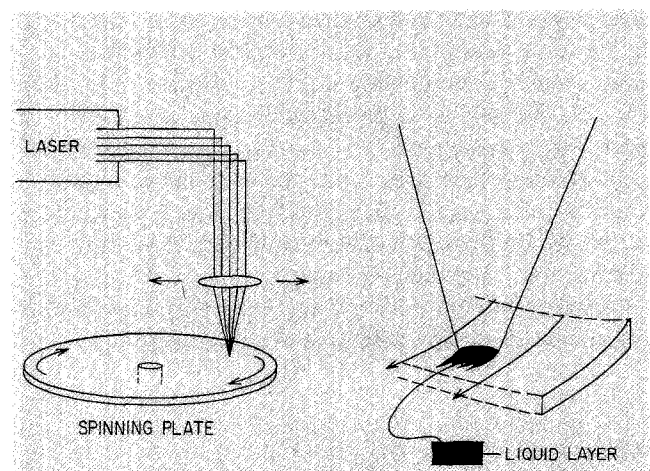
How would one go about actually cooling something fast enough to do this? About 20 years ago here at Caltech, Professor Pol Duwez showed that by rapidly cooling a liquid metal, by sandwiching it between two highly conductive pieces of cold metal and "splating" it out into thin foil, it is possible to retain this glassy structure. A radio-frequency coil heats the liquid metal in a crucible. When a drop of liquid metal falls, it triggers a detector, and the falling drop is captured by a piston, which impacts at a very high velocity, literally splatting the drop between two copper surfaces. Copper is a very good conductor of heat. If you spread the drop out and make it thin enough, it takes very little time to remove the heat. The metal can be cooled at the rate of a million degrees per second.

To deform an object made of metallic glass would be extremely difficult for two reasons. The carbon (boron) atoms bond with the neighboring iron atoms like little braces and make the structure very rigid. Also since the atoms are no longer periodic in space, there is no direction along which the metal can give easily; that is, there are no slip planes along which the material deforms easily as it did in the case of crystalline iron. In the crystal, carbon atoms lock up the iron, but the crystal can still slip along the plane. Now we have even gotten rid of that problem. There is no preferred direction for the slip to occur.

The strength of many iron-base metallic glasses is between 400,000 and 500,000 psi. As mentioned earlier, the strength of pure iron is 50,000 psi, and a very high carbon steel is 150,000 psi. In a technological sense, we've made a leap forward in improving the strength of these materials. We've found a method of getting a high carbon concentration everywhere in the sample. This process produces a uniform, homogeneous material in contrast with techniques that add carbon to the surface only.

Of course, if you want to apply this technique to a practical problem, you are immediately faced with the question

Laser glazing can create a glassy metallic surface by melting the skin of a material and cooling it at a million degrees per second.

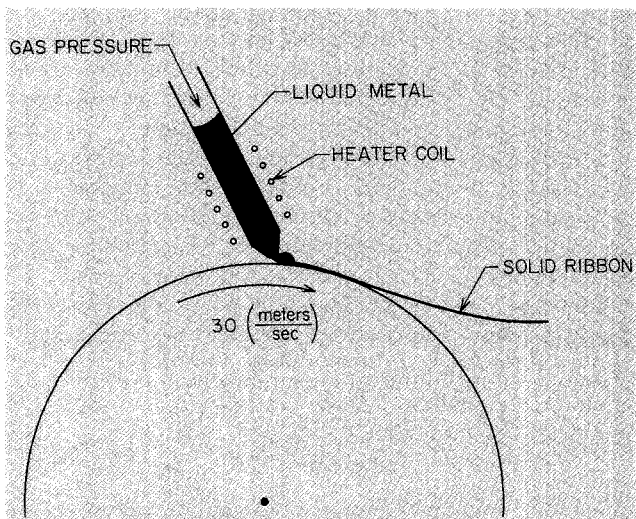


of how to produce a useful material in sufficient quantity by slapping drops between two plates. Such a process would not yield enough material to serve most practical applications. So the next obvious hurdle was to figure out how to cool metal with a lot of carbon or boron in very large quantities at a million degrees per second. Some of the ways this is currently being done incorporate technology that has been developed in the last decade.

One process employs a laser. Laser light is focused to a very fine point on a plate spinning at a very high velocity. As the material spins by and passes under the laser beam, it's melted very quickly, forming a little liquid pool on top of the cold plate. As this passes out of the laser beam, we have the same sort of situation as the drop being spread very thin over a copper surface. With the laser technique, the heat is conducted very rapidly into the material itself. The plate below the liquid skin remains cold, so the material solidifies very rapidly. With this technology a cooling rate of a million degrees per second can again be achieved, and an amorphous or glassy layer two or three thousandths of an inch thick can be made on the surface of a metal object. This is useful for making objects that resist wear well. Unfortunately, we're still on the surface, even though in a better position than with ion implantation since with that process we were limited to much thinner layers.

The Allied Chemical Corporation pioneered a new technology back in about 1971 and 1972, in which they studied the formation of metallic glass using what is called a melt spinning technique. In melt spinning the metal is melted with a radio frequency coil or heater coil, and gas pressure then forces the liquid metal onto a wheel that is rotating at extremely high velocity, say a surface speed of 30 meters per second or about 60 miles per hour — like a car down a freeway. The metal is pulled off by the rotating wheel into a thin layer and spun off as a ribbon. Miles of it can be produced in a very short time. This process works

Melt spinning produces metallic glass ribbon in large quantities drawn off and cooled by a rapidly rotating wheel.



extremely well, and the formation of a melt puddle with the ribbon coming off is an extremely stable configuration. An iron-based alloy or steel can be continuously cast at the rate of a million degrees per second.

These materials are extremely interesting from a technological point of view. General Electric Corporation is now fabricating ribbons of amorphous iron alloys that have very interesting magnetic properties. Cross-country power transformers step up the voltage on transmission lines to allow electrical power to be distributed over large distances. These are currently made from a crystalline alloy of iron and silicon; it's a very expensive material to produce and requires a lot of processing. The amorphous alloy spun off the wheel is a much better magnetic material for this application because it's magnetically softer. This means that the transformer made of metallic glass ribbons would dissipate less energy. In fact, you can reduce the power loss from the transformer by as much as a factor of 10. Since a significant amount of electrical power is lost every time power passes through one of these transformers, reduction of the loss could save hundreds of millions of dollars worth of energy every year. General Electric hopes to replace cross-country power transformers with transformers made from metallic glasses, by simply winding up ribbons to make transformers.

There are a number of other interesting applications and a variety of other unusual properties, some of which we're currently studying here at Caltech. Metallic glasses resist corrosion extremely well — much better than stainless steel. Many of the metallic glasses become superconducting at low temperatures. A superconducting material is a metal that at temperatures near absolute zero loses all its resistance to the flow of electricity. Many crystalline metals also have this property, but the glassy superconductors, such as alloys of molybdenum-ruthenium-boron, remain superconducting in extremely high magnetic fields. This is a very useful property in the construction of superconducting magnets and the building of magnets that will generate very large magnetic fields. The metallic glasses are also extremely strong and have very desirable mechanical properties. Crystalline materials that are good superconductors on the other hand don't generally have desirable mechanical properties.

Our group at Caltech is currently involved in research on many diverse aspects of metallic glasses. This is still a comparatively new field, and the technological impact of these materials is just now beginning to be felt. It's very probable that in the coming years the number of applications for these materials will expand at an exponential or geometric rate. □